Highly fluorinated organic compounds: analytical measurements in the environment and in the work-place

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February 9, 2011

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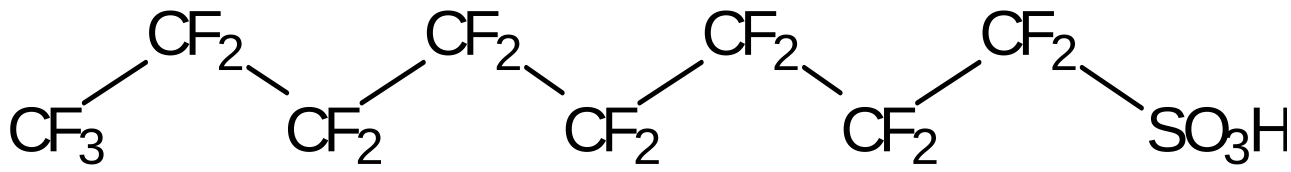
Outline

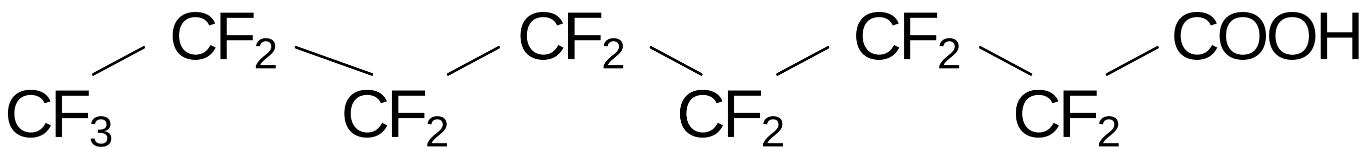
- Structures and terms
- Product applications
- Uniqueness of carbon-fluorine bond
- Effect of unique C-F bond on measurements
- Examples and applications
- Discussion

Important structures

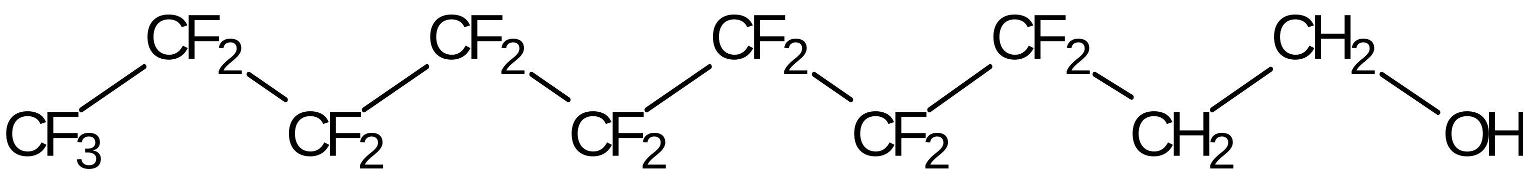
PFOS



PFOA



8:2 Fluorotelomer alcohol (8:2 FTOH) (an intermediate)



Product Applications
DuPont Brand Terminology

Teflon® is a brand used to identify articles meeting DuPont performance certification criteria.

- Many different DuPont products and product chemistries are used to create Teflon® branded articles. Teflon® is not PFOA.

Zonyl® / Forafac® / Foraperle® / Capstone® are product trade names for DuPont Fluorotelomer & Fluoropolymer based products.

- Some end-use articles treated with or containing Zonyl® or Capstone® products are branded Teflon®.

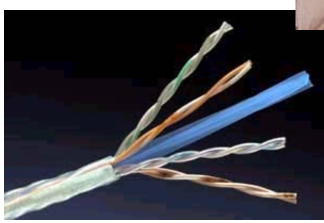
New Chemistries

- DuPont is committed to phase out the use and production of PFOA by 2015 or earlier, if possible, and to develop new products and processes that are more environmentally sustainable.

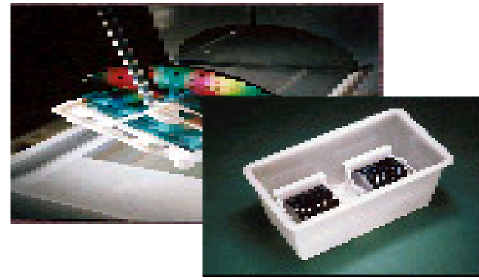
- Our corporate phase out commitment has helped promote the rapid transition to a new generation of products and processes that have a reduced environmental footprint, and do not sacrifice product performance.

Product Applications – Fluoropolymer Resins

Material Properties



Telecomm
Wire & Cabling



Semiconductor Manufacture

High Purity
Liquid Handling

Chemical Processing
Valves, Lined Piping, Tanks

Aerospace Materials
Hydraulic tubing
Wire & Cabling Flares

Low Permeable
Automotive Fuel Hose

DuPont

Product Applications
Fluoropolymers

Fluoropolymers (e.g., polytetrafluoroethylene, PTFE) are high molecular weight polymers with the inherent properties of chemical resistance and thermal stability which cannot be achieved with any other known substances.

- **They have high thermal stability, are non-flammable and are resistant to chemical attack in addition to having low friction (e.g. slippery) and excellent electrical insulation properties.**

Certain fluoropolymers are manufactured using perfluorooctanoic acid (PFOA) as a polymerization processing aid.

- **Perfluorooctanoic acid (PFOA) is neither reacted with nor incorporated into the fluoropolymer.**
- **A variety of processes, including high heat treatment, are used to reduce PFOA content to trace levels in final products.**
- **DuPont and several other companies have developed and are beginning to use new polymerization processing aids that allow the manufacture of fluoropolymers without the use of PFOA.**

Product Applications - Fluoropolymer Dispersions

Material Properties

Construction Architectural Fabric

Non-stick Coatings for Cookware and Small Electrical Appliances

Product Applications

Fluorotelomers

- Fluorotelomers are used to produce surface protection products, including surfactants and repellents, for a wide range of applications in home furnishings, textiles, paper, fire-fighting foam, nonwovens, coatings, and stone and tile protection.
- Fluorotelomer-based products have been produced by DuPont for more than 35 years.
- Because of their unique characteristics, fluorotelomers are widely used where dependable performance is essential.
- The products and applications listed above bring consumers many benefits, which include ease of care, reduced maintenance, and extended life for a broad range of articles used every day.
- Fluorotelomers are sold under the following brands: Teflon®, Zonyl®, Foraperle®, Forafac® and Capstone® Products.

Product Applications – Fluorotelomers
Surface Modification

Industrial Fire Fighting

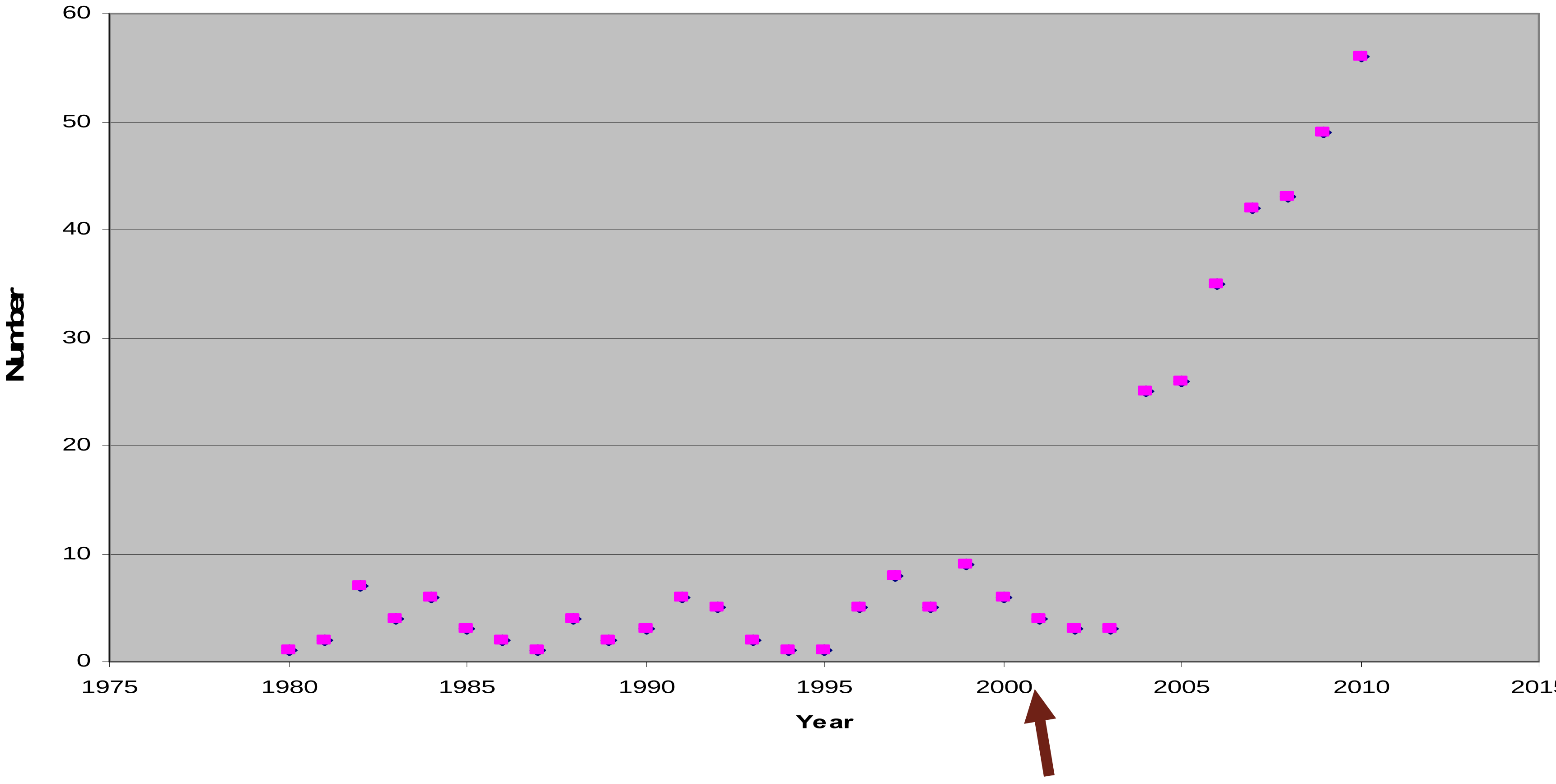
Architectural Coatings and Sealers

Carpet & Textiles

Health Care

Grease Resistant Packaging

Peer-reviewed publications: perfluorocarboxylic acids and fluorotelomers



Hansen *et al.*, 2001

Number of published papers by topic

TOPIC	2008	2009	2010*	% Papers	Trend
Analytical	19	31	3	7	↓
Environmental Effects	14	14	11	5	↑?
Environmental Exposure	76	97	29	28	—
Degradation	14	23	6	6	—
Human Exposure	21	28	10	8	—
Mechanism of Action	8	16	13	5	↑
Pharmacokinetics	7	20	9	5	—
Reproduction/Developmental	11	15	4	4	—
Toxicology - General	66	78	29	24	—
Human Toxicology	8	40	8	8	↓?
Total	244	362	122 (366)		

* 4 months data

Uniqueness of fluorinated compounds: F_2

Elemental Fluorine (F)

- most electronegative element (401 kcal/g-atom)
- most chemically reactive of all the elements

Uniqueness of fluorinated compounds: C-F

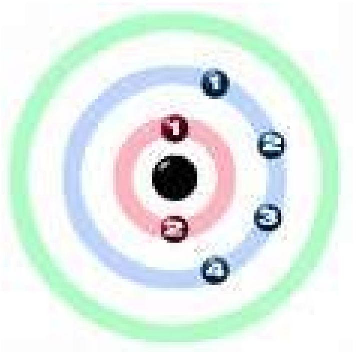
Bond energy

C-F	116 kcal/mole
C-H	99 kcal/mole
C-Cl	79 kcal/mole

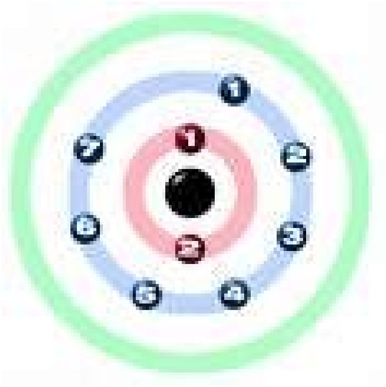
Pyrolysis

Fluorocarbons tend to split the C-C bond rather than the C-F bond

C



F



Uniqueness of fluorinated compounds: C-F

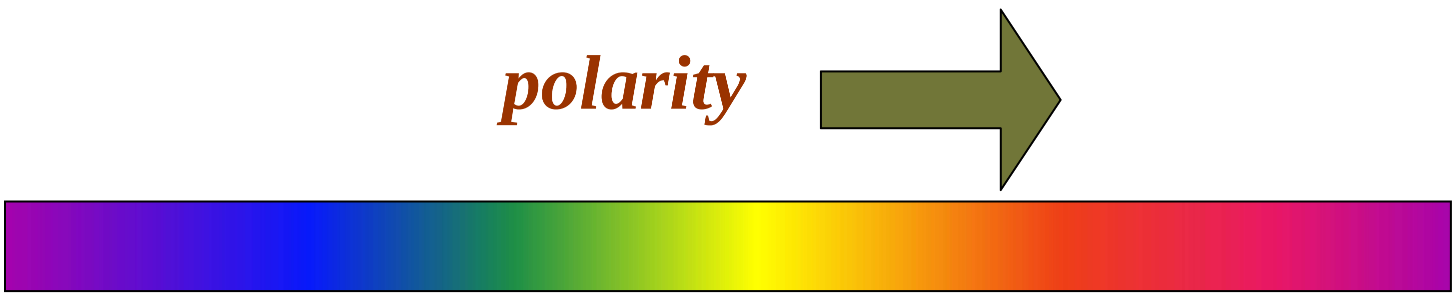
"Many of these compounds have chemical and physical properties strikingly different from the hydrogen analogs or from analogous compounds of the other halogens where they exist."

<u>Advanced Inorganic Chemistry</u>, F. A. Cotton and G. Wilkinson, Interscience Publishers, New York, 1966.

Extreme hydrophobicity and significant oleophobicity of the perfluoro chain

Solvatochromic π scale is an index of solvent dipolarity and polarizability

polarity



-0.41	0.00	0.55	1.09
perfluorooctane	cyclohexane	ethyl acetate	water

M. J Kamlet, J-L Abboud, M H Abraham, R W Taft, ***J. Org. Chem.***, **1983**, *48*, 2877-2887.

What work has to be done?

To improve sensitivity and specificity for physical property and analytical measurements in complex and diverse matrices.

To determine environmental fate and effects on products and residuals

- Hydrolysis
- Partitioning behavior
- Photolysis
- Atmospheric studies
- Biodegradation

Why are physical property measurements so important?

- Needed for environmental fate and transport modeling.
- Needed to understand approach to environmental monitoring, including sampling and analytical method development.
- Essential for risk assessment.

Which physical properties are important?

- Aqueous solubility
- Vapor pressure
- Sorption coefficients on soil, particulates, sludge, sediment
- UV/VIS spectrum
- Sublimation propensity (rate, enthalpy of sublimation)

Where can physical property data be obtained?

- **the literature** (perhaps)
- **modeling programs** (do not work well for F-containing compounds)
- **direct or indirect measurement**
  - in range of measurement
  - extrapolated from measured data
  - determined relative to “known” materials

Are literature values reliable?

- **Need to look at the details of the experiment**
- **Need to consider the circumstances and knowledge at the *time* of the measurement**
- **For example**
  - how was the material characterized?
  - were known standards run?
  - were isomers or impurities considered?
  - was the measurement direct or relative?
  - how accurate, precise, robust was the measurement?

Solubility of 8:2 FTOH

Molecular weight: 578 g/mole

Vapor Pressure: 7 Pa at 25 °C

Solubility in water: ~150 ppb at 25 °C*

What is solubility?

*"Physicochemical Properties of Telomer B 8-2 Alcohol", Mary A. Kaiser, Daryl P. Cobranchi, Chien-Ping Chai Kao, Paul J. Krusic, Alexander A. Marchione, Raymond E. Richardson, and Robert C. Buck, *J. Chem. Eng. Data*, **49**(4); 912-916 (2004).

Solubility

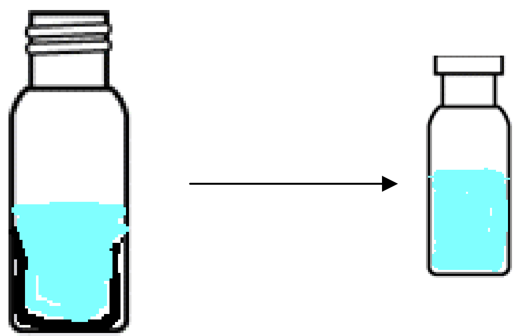
The amount of mass of a compound that will dissolve in a unit volume of solution.

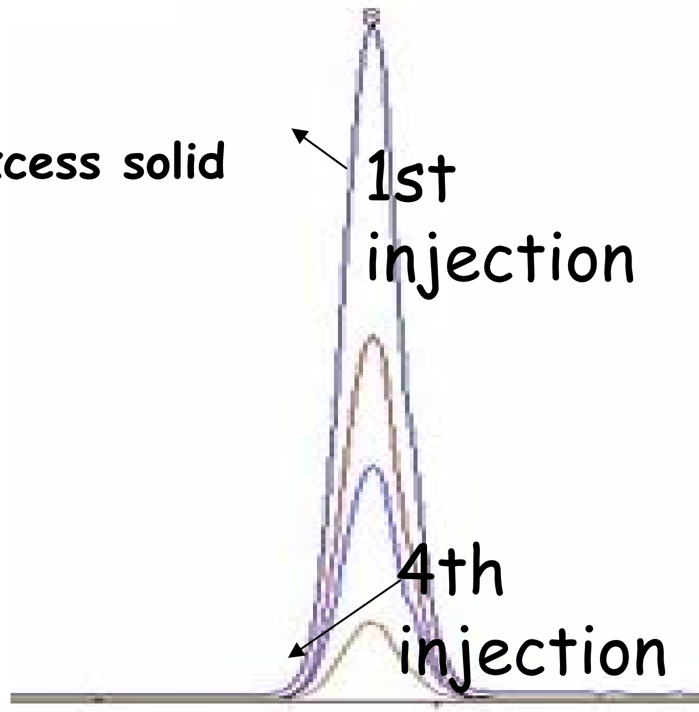
(US EPA definition)

There are numerous "standard methods" for solubility determination. (US EPA, OECD, US FDA, ASTM)

Water solubility of 8:2 FTOH*

- Saturated aqueous solution with excess solid in vial
- Shake for 24 hours
- Either filtered or centrifuged to remove excess solid
- Place in GC vial
- Four consecutive injections, GC/FID





*Kaiser *et al.*, *J. Chem. Eng. Data*, **2004**, 49, 912-916.

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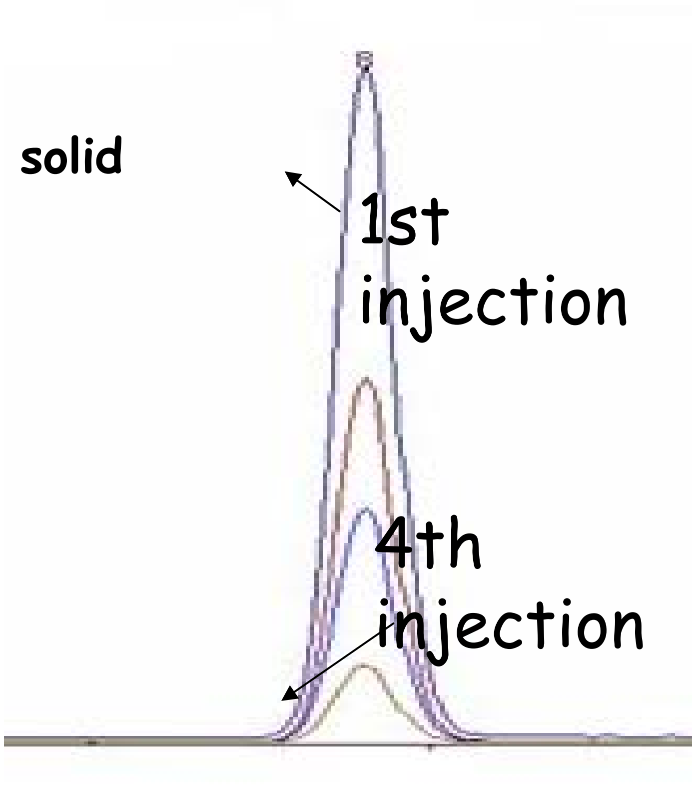
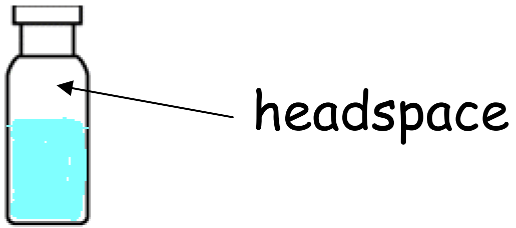
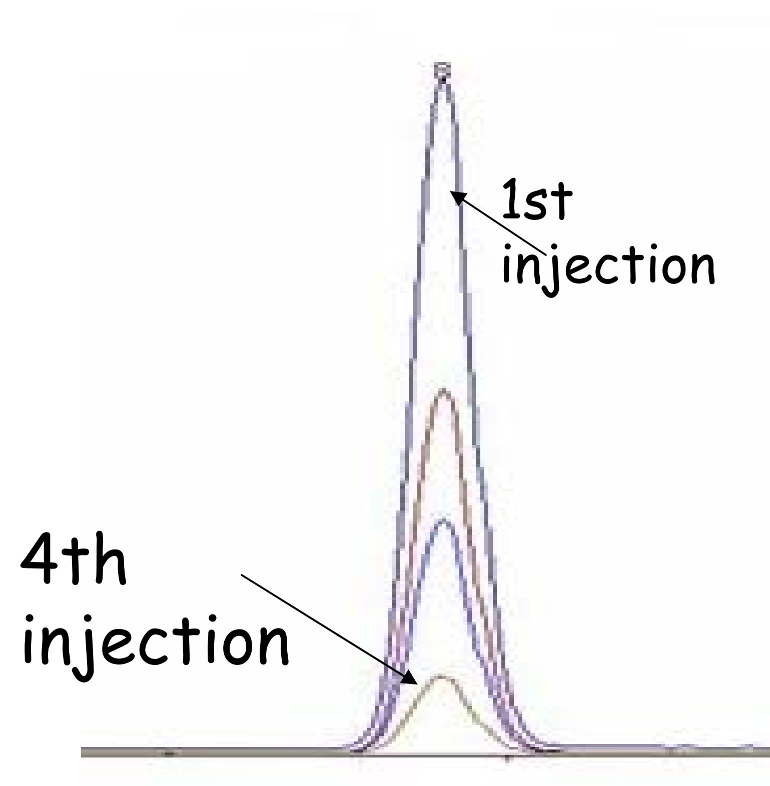


*Kaiser *et al.*, *J. Chem. Eng. Data*, **2004**, 49, 912-916.

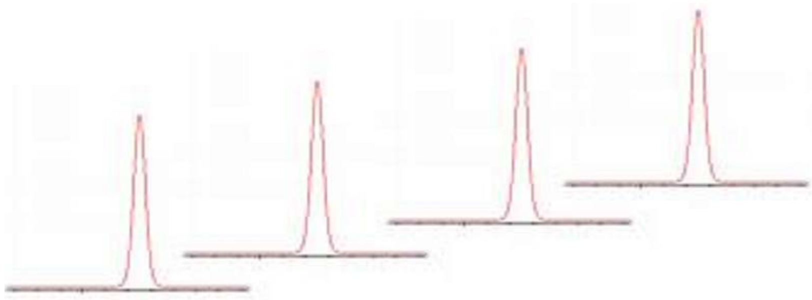
Water solubility of 8:2 FTOH*





New water solubility method for 8:2 FTOH*

- Saturated aqueous solution with excess solid melted onto walls of vial
- No headspace
- Aluminum foil liner
- Shake for 24 hours
- Four consecutive injections, GC/FID



Water solubility ~150 ppb????
The value we measure is a "limiting" value.

What else do we know about 8:2 FTOH?

8:2 FTOH sorbs rapidly and strongly to soils, sediments and sludge, irreversibly, with increasing time.

Liu *et al.*, ES&T, 2005

So, is aqueous solubility a relevant parameter to determine long range transport in the environment?

So, is aqueous solubility a relevant parameter to determine long range transport in the environment?

Yes. But other physical phenomena must be considered to understand what happens in the environment.

Analytical determinations

How have analytical methods evolved?

What type of analytical methods were typically in use before May 2000?

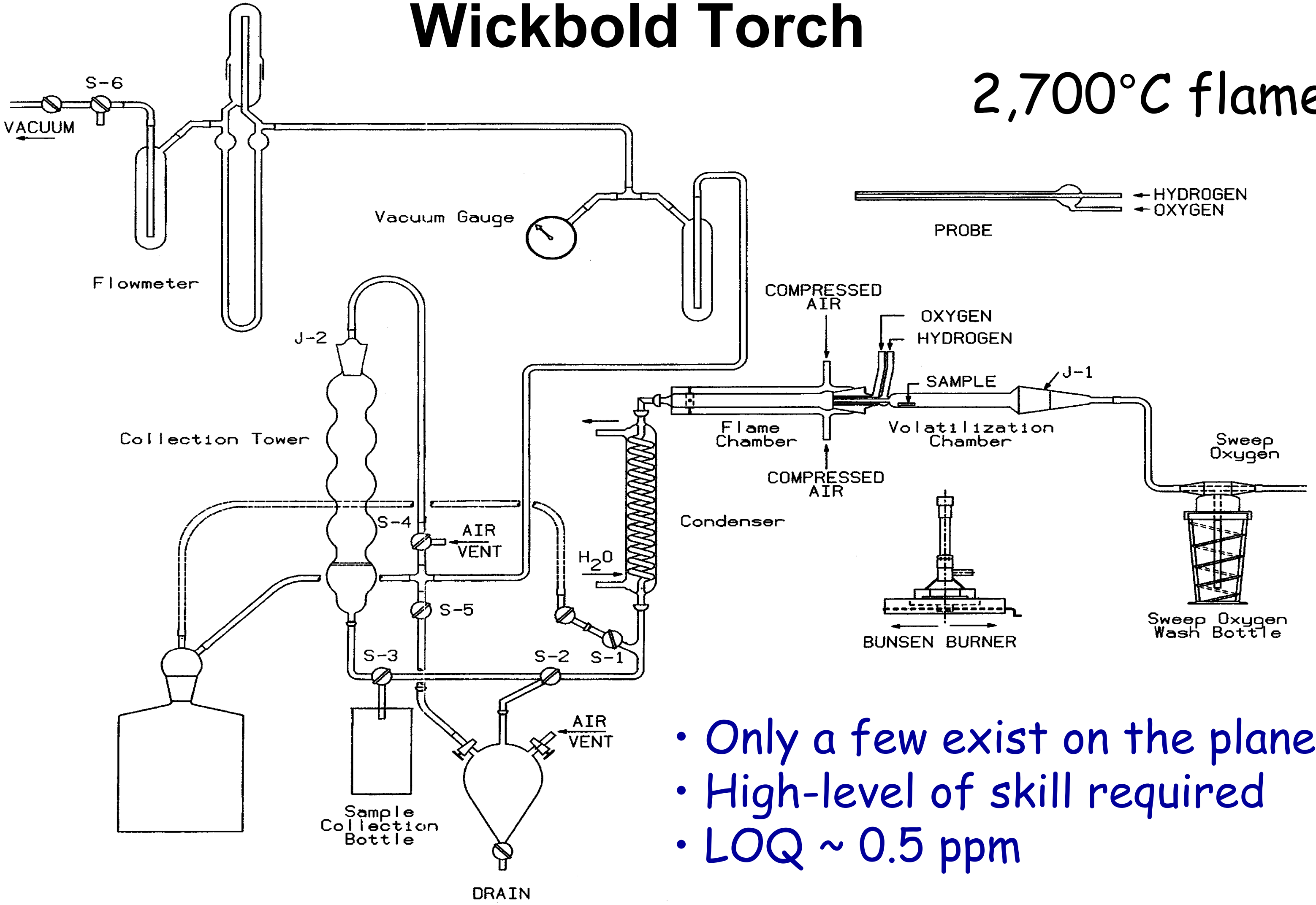
Wickbold torch for elemental F analysis

GC/ECD for volatile (or those that can be made volatile) compounds

an old GC

Wickbold Torch

2,700°C flame T

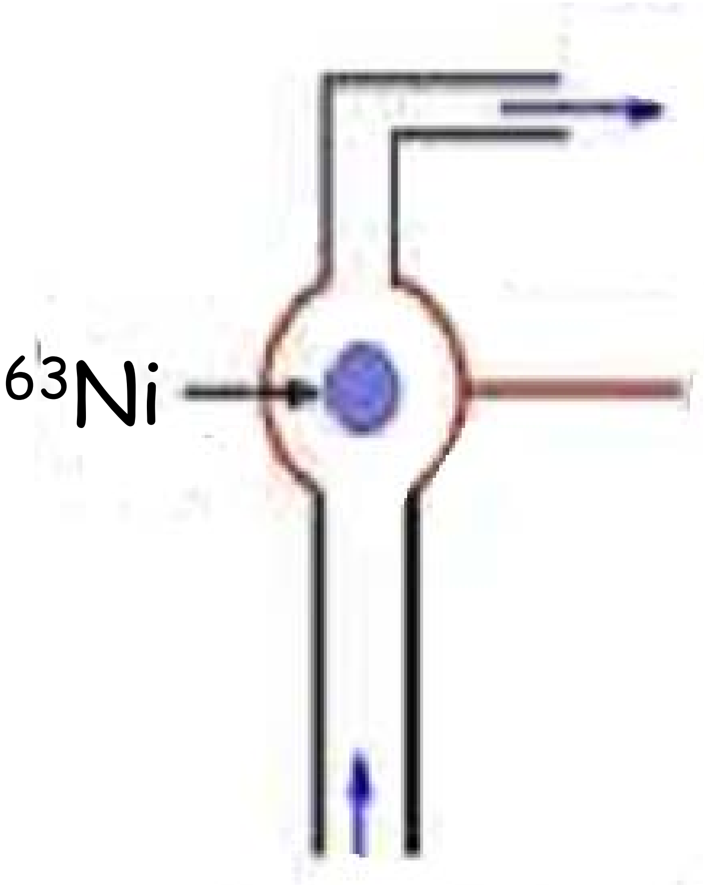


- Only a few exist on the planet
- High-level of skill required
- LOQ ~ 0.5 ppm

Wickbold,R., Angew. Chem., 64 (1952) 133.

Gas chromatography/electron-capture detector (GC/ECD), late 1970s

- Nonlinear
- Nonspecific
- Not much better than GC/FID for this application *(fluorine has a small cross-sectional area)*



LC/MS/MS

Hansen *et al.*,*Environ. Sci. Technol.*, **35**, 766-770 (2001).

"Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices"

PFOS, PFOA, PFHxS, PFOSA*

LC API ES (negative ion mode) MS/MS

*perfluorooctanesulfonate, perfluorooctanoic acid, perfluorohexanesulfonate, perfluorooctanesulfonylamide

Advantages/disadvantages LC/MS/MS vs. GC/ECD

LC/MS/MS has greater sensitivity (i.e., lower LOD/LOQs)

and better selectivity (e.g., for PFO, look at loss of COO, then CF_2COO)

But co-eluted peaks may attenuate or enhance LC/MS/MS signal

and perfluorooctanoate may be present in background (especially PFOA in solvents and perfluoropolymer parts)

Early issues affecting quantitative analysis

No true analytical standards existed

- had to characterize reagents first by multiple analytical techniques

No isotopically enriched standards to use as internal standards and surrogates

Two synthetic methods were used to make perfluorocarboxylic acids

- electrochemical fluorination (ECF) or
- perfluorooctyl iodide oxidation

gave different impurities

- Issue: do you add the linear with the branched from the ECF process?

Solutions to early problems

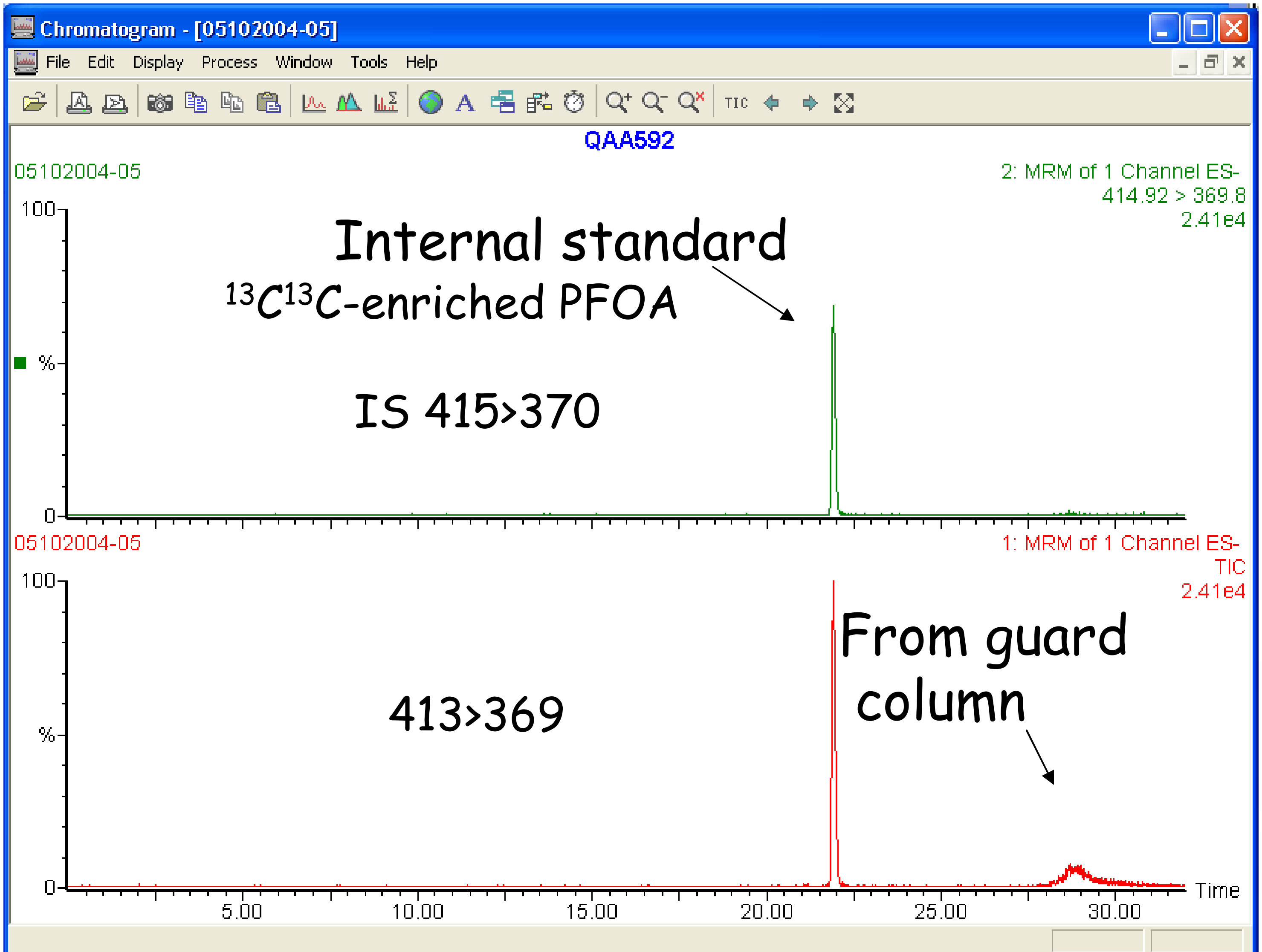
Commercial labs eventually made ^{14}C and m +2 and m+4 (^{13}C) perfluorooctanoate standards

(great synthesis effort)

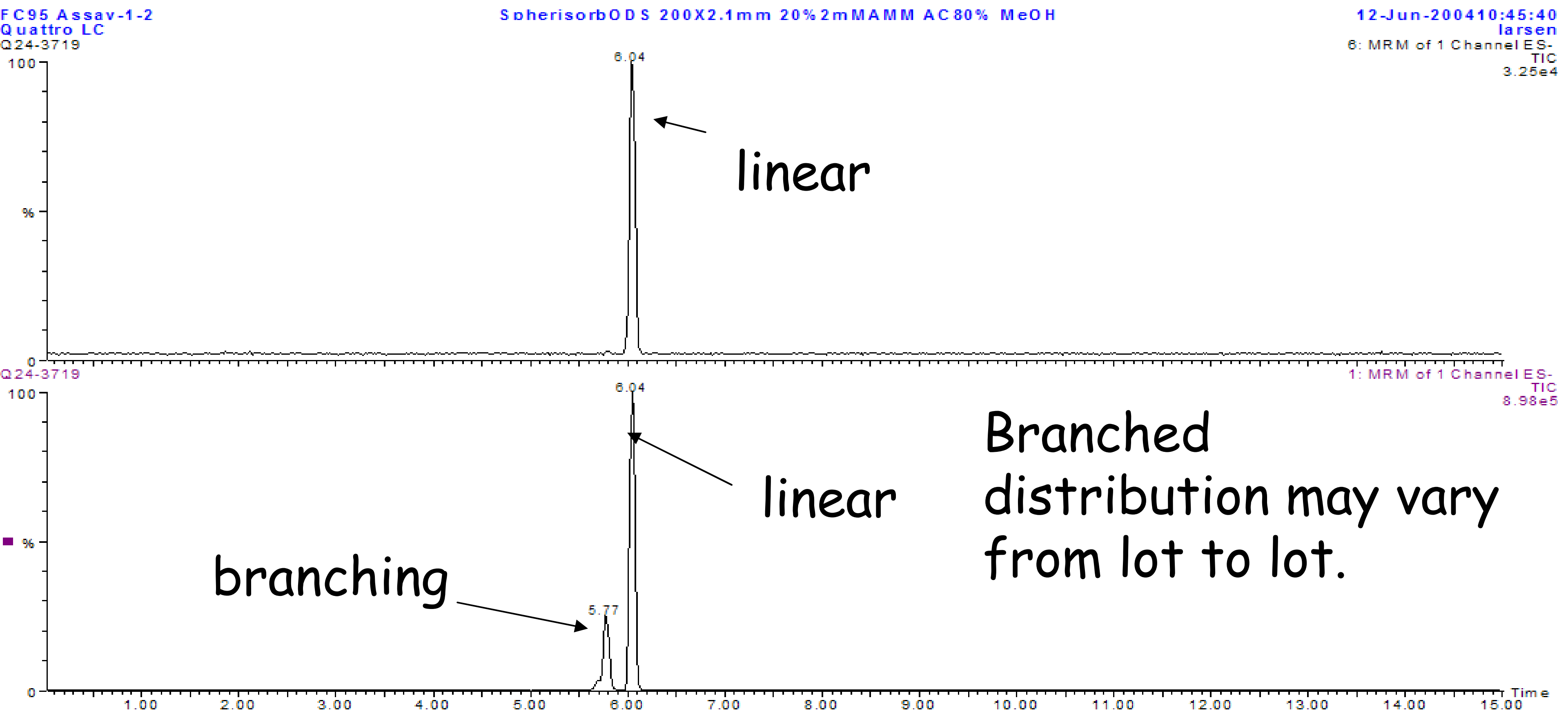
Guard columns could be used for gradient runs*

* Risha *et al.*, *Anal. Chem.*, 2005, 77, 1503-1508.

Guard Column
Useful in gradient measurements

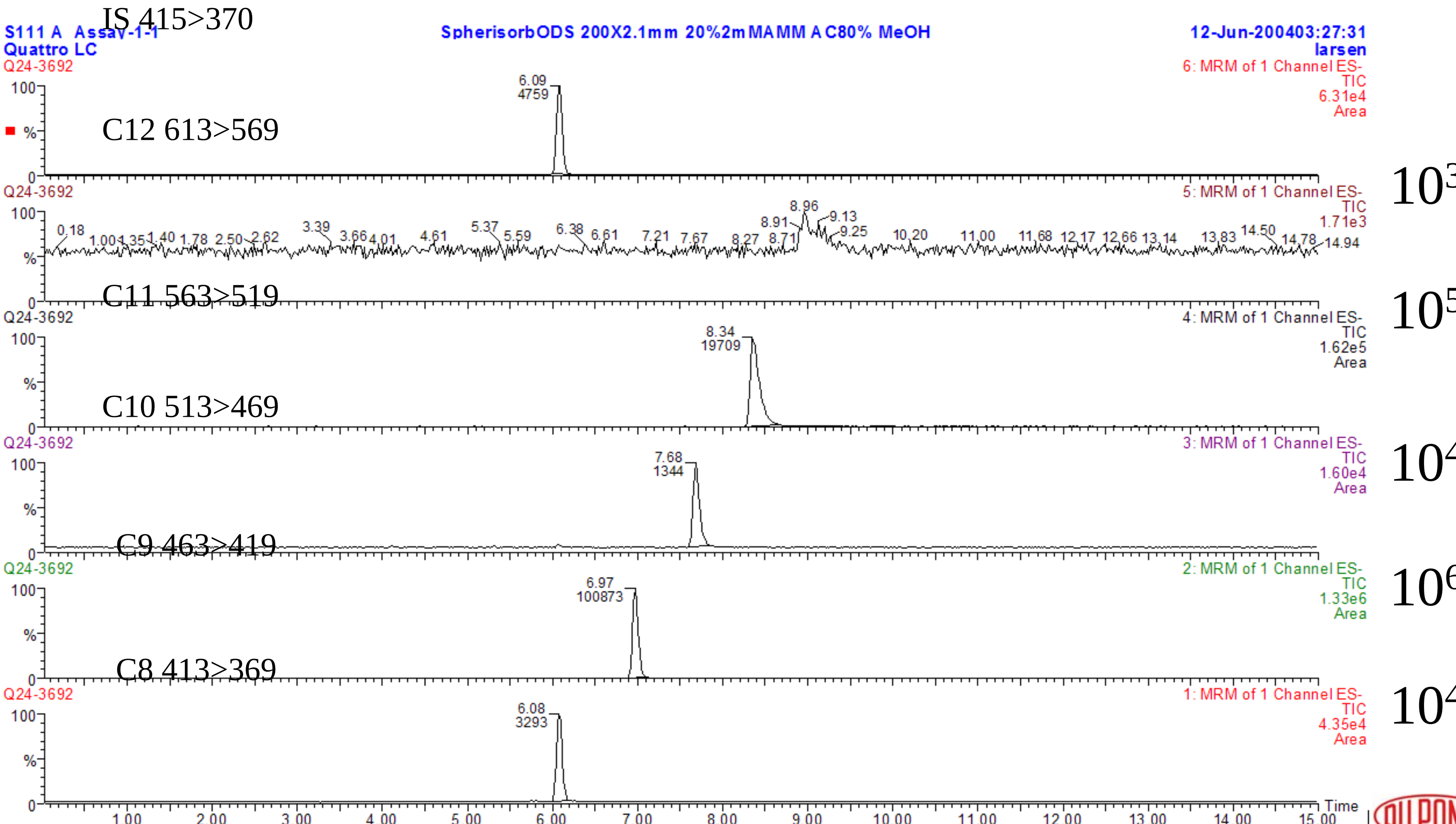


“Standards?”
Perfluorooctanoic acid produced by perfluorooctyl iodide oxidation or electrochemical fluorination



"Standards?"
C9: "Perfluorononanoic acid" (Surflon® S111)

Contains 9, 11 and 13 carbon acids



Let's consider a practical application of LC/MS/MS

Given: ammonium perfluorooctanoate (APFO) is often used as a fluoropolymer processing aid in the manufacturing of polytetrafluoroethylene (PTFE)

and PTFE usually goes through a sintering process above the temperature where APFO decomposes

Determine if any residual (low-level)APFO remains in a commercial fry pan.

Note: the anion perfluorooctanoate (PFO) is measured in the LC/MS/MS experiment.

$$PFO = CF_3CF_2CF_2CF_2CF_2CF_2CF_2COO^-$$

Water extract from coated fry pan

- 11 fry pans (5 SS and 6 coated)
- Washed via manufacturer's suggestion
  - ~ 600 mL water
  - reflux 30 min
- 40 mL aliquot concentrated on C_{18} SPE column; eluted with 5 mL methanol
- Determination via LC/ESI/MS/MS

Water extract from coated fry pan

Perfluorooctanoate <u>not detected</u>

- Water reflux of fry pans resulted in non-detect for PFO (LOD = 50 pg/cm^2)
- One of the water samples from a SS pan gave a quantifiable amount near the LOQ. Follow-up samples gave ND.

Water extract from coated fry pan

Perfluorooctaaoate <u>not detected</u>

- Fry pan cut up into strips followed by PSE
- Extraction of fry pans using ethanol/water in pressurized solvent resulted in non detect (LOD = 100 pg/cm^2)

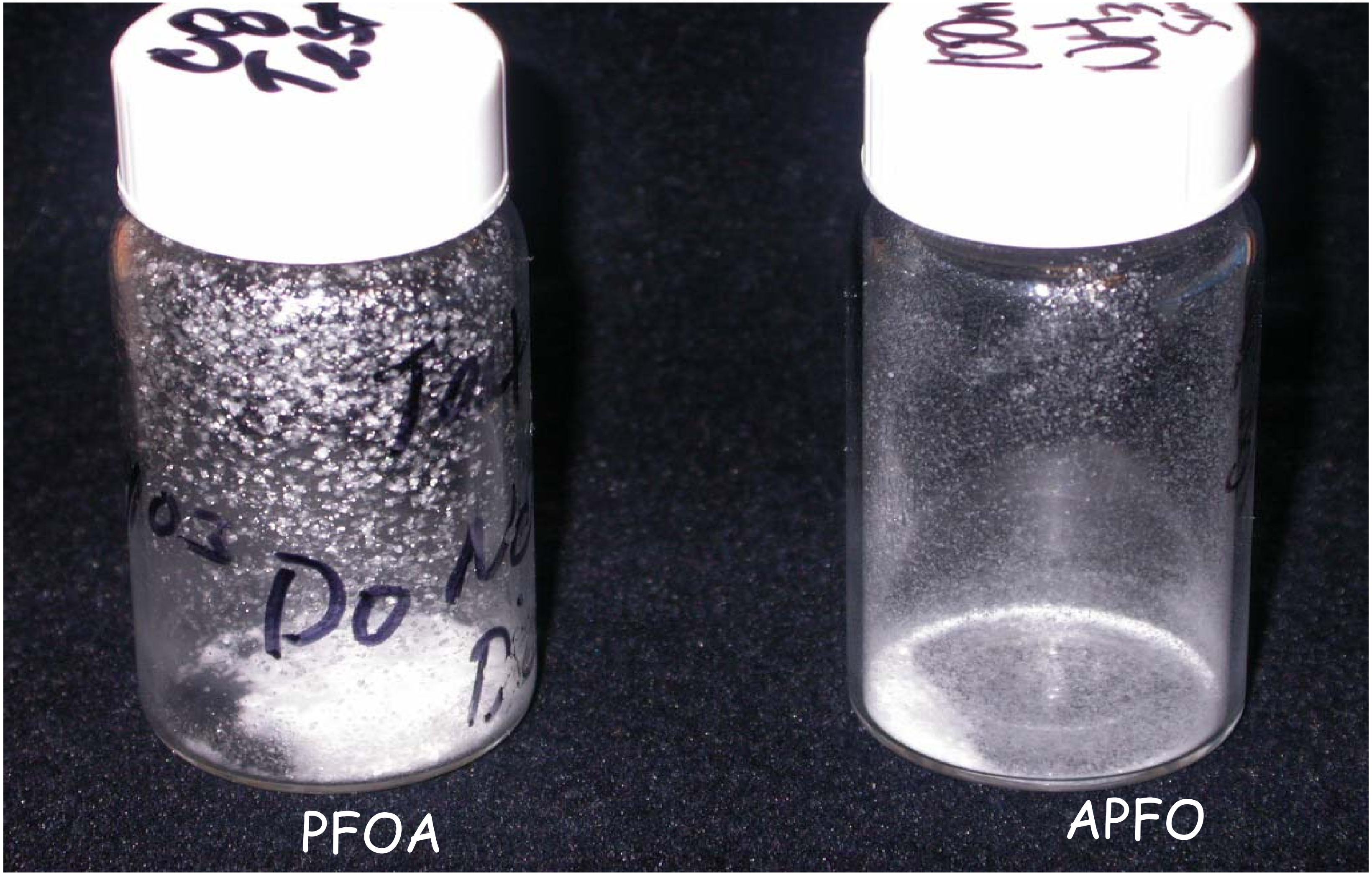
Some examples of difficult matrices...

Coated paper

- goal LOQ 1 ng/g (ppb) for PFOA
- Physical properties: MW 414, VP 128 Pa at 60 C, water solubility 4 g/L at 22 C
- problem: high blanks (untreated paper)
- *aha!* that led to problem solution
  - found that if we took a paper from the middle of the copier stack, got ND for analyte
- Why?

Sublimation

Evidence of sublimation of PFOA and APFO



How has physical property knowledge and reliable analytical determinations helped us understand potential exposure ?

Eight-hour time-weighted average air levels of PFOA near process sumps

Day	PFOA (mg/m^3)	Comment
1	0.065	Low pH sump
1	0.007	After sump pH adjusted to 7
11	0.061	Low water in sump
13	0.004	Water level restored

Summary

- The C-F bond has a large impact on how molecules behave.
- Cannot use knowledge of halocarbons or hydrocarbons to infer properties for highly fluorinated substances.
- LC/MS/MS is a great analytical technique but good chromatography is very important component.
- Many method blanks and spikes are essential.
- Pay close attention to sample preparation techniques to avoid contamination.
- Use mass-labeled (e.g., ^{13}C) chemical standards.

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Thank you!

- **Questions**
- **Comments**
- **Discussion**

February 9, 2011

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